

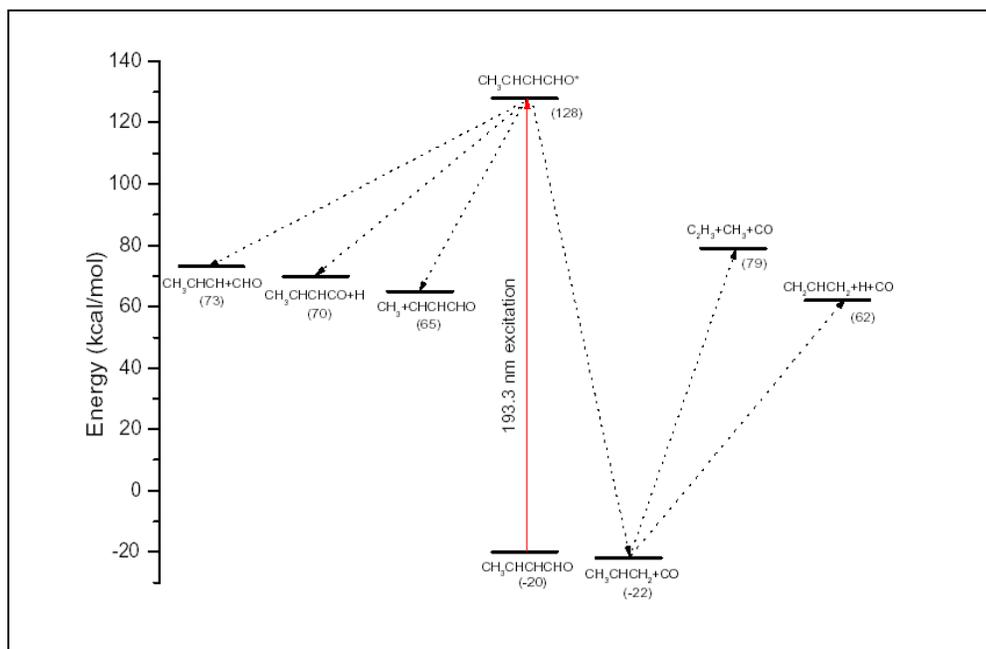
Photofragment translational spectroscopy using tunable synchrotron radiation

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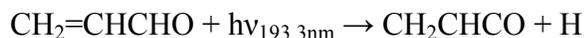
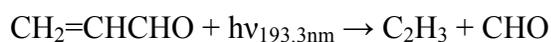
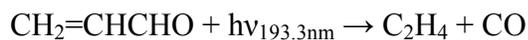
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During 2002, we carried out the photodissociation of crotonaldehyde ($\text{CH}_3\text{CHCHCHO}$) with 193.3 nm laser light at ESI using the technique of photofragment translational spectroscopy¹. As we know, carbonyl compounds are very important precursors of radicals in the atmosphere and these experiments aids our understanding of their photochemistry. To date there have been only a few end-product analysis experiments on crotonaldehyde². The use of tunable undulator radiation provided the unprecedented ability to identify a range of hydrocarbon radical fragments directly. This is very important when we study the photodissociation of large molecules which give rise to multiple dissociation products and complex mechanisms. In the photodissociation experiment of crotonaldehyde, we observed four primary dissociation channels: $\text{H} + \text{C}_4\text{H}_5\text{O}$, $\text{CH}_3 + \text{C}_3\text{H}_3\text{O}$, $\text{CHO} + \text{C}_3\text{H}_5$, and $\text{CO} + \text{C}_3\text{H}_6$. We measured the translational energies of the various products.



Acrolein (CH_2CHCHO), the smallest unsaturated carbonyl compound, is the analogue of crotonaldehyde and its photodissociation dynamics can serve as an aid in understanding the dynamics of crotonaldehyde photodissociation. The structural difference between the two molecules is that crotonaldehyde has one CH_3 group instead of one hydrogen atom on the α carbon atom of acrolein. Compared with crotonaldehyde, acrolein has attracted more attention and extensive studies on its photodissociation have been performed³. The UV-visible absorption spectra of acrolein is very similar to that of crotonaldehyde and just shifts about 5 ~ 10 nm to the blue side. The following three primary channels have been observed in the case of acrolein:



Our results show that crotonaldehyde shows similar behaviour to acrolein. Besides the rupture of single bond during the photodissociation, the process of H atom migration is also interesting, which results in the molecular products CO and C₃H₆. The experimental results also indicate that C₃H₆ undergoes a strong secondary dissociation. We are still in the process of understanding the complex dissociation mechanisms that crotonaldehyde undergoes upon photoexcitation at 193 nm.

In addition, we have also performed photodissociation studies of acetic acid at 193 nm. We observed two primary channels: OH + CH₃CO, and CH₃ + COOH. The OH loss channel is the dominant channel. These experimental results show the partial products of CH₃CO leads to secondary dissociation due to higher internal energy deposition.

REFERENCES

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